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(54) Title: INHIBITED ALKYLENE GLYCOL COOLANT AND COOLING PROCESS**(57) Abstract**

A coolant composition containing (1) an alkylene glycol such as propylene glycol, (2) a corrosion inhibitor combination of an azole such as tolytriazole, a molybdate salt and phosphoric acid and (3) less than 10 weight percent of water exhibits high temperature stability and corrosion inhibition for metals used in internal combustion engine cooling systems, particularly such metals as aluminum and magnesium and a process of cooling such an engine.

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INHIBITED ALKYLENE GLYCOL COOLANT
AND COOLING PROCESS

This invention relates to corrosion inhibited alkylene glycol compositions useful as coolants for the heat-exchange system of an internal combustion engine 5 and to the process of using same to cool such an engine.

Presently, antifreeze compositions containing 10 alcohols, especially ethylene glycol, are commonly mixed with equal or larger volumes of water in the cooling systems of internal combustion engines in order to depress the freezing point of the water. Such alcohols, in combination with the water in the cooling systems, 15 produces acidic products which contribute to the corrosion of metal surfaces that contact the cooling system. Thus the uninhibited antifreeze compositions promote corrosion of brass, copper, solder, steel, cast iron and in more recent engines, aluminum and magnesium. 20

In the past a large number of corrosion inhibitors and combinations thereof have been employed in 25 such aqueous-base antifreeze compositions. Such

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inhibitors have included the alkali metal chromates, nitrates, phosphates, borates, tungstates, molybdates, carbonates and silicates and alkaline earth metal borates. Inhibitors have also included organic compounds such as carboxylic acids, thiocyanates, phenols, mercaptans, mercaptothiazoles and various aromatic tri-azoles. Many of such inhibitors, such as the silicates, deplete quickly and are no longer available for continued metal protection. Others, such as 5 nitrates, which function well as inhibitors against the 10 corrosion of iron or steel actually promote the corrosion of aluminum or magnesium.

Recently in an attempt to develop an improved 15 cooling system from the standpoint of fuel efficiency and cooling efficiency, a cooling process was developed which employed a coolant containing little or no water. U.S. Patents 4,550,694 and 4,630,572. The primary 20 means by which this system achieves the improvement in engine efficiency is to run the engine at higher than normal engine temperatures. Such higher temperatures often degrade many of the corrosion inhibitors such as the silicates at an even faster rate. Also, it has 25 been found that uninhibited glycols used as anhydrous coolants are corrosive to typical cooling system components.

Therefore it is highly desirable to provide an 30 inhibited coolant composition which is capable of functioning at temperatures in excess of 105°C, but which will not corrode the metal which is commonly used in the cooling systems of internal combustion engines.

The present invention is such a composition which comprises (1) at least 90 weight percent of an alkylene glycol or a mixture of two or more alkylene glycols and (2) a corrosion-inhibiting amount of an inhibitor comprising (a) from 0.02 to 4 weight parts of 5 an azole, (b) from 0.05 to 3 weight parts of a molybdate salt and (c) from 0 to 3 weight parts of phosphoric acid. It also is a process of cooling an internal combustion engine by circulating said 10 composition, as coolant, through the cooling jacket of said engine.

By employing (1) alkylene glycol as at least 90 weight percent of the coolant and (2) the 15 aforementioned combination of corrosion inhibitors, metals such as aluminum and magnesium can be used in components, e.g., radiator, coolant pump, engine block, cylinder head, of the cooling system. The coolant composition can be employed in engines operating at 20 temperatures higher than normal without degrading. As a result the engines are more fuel efficient and produce combustion products that are less offensive to the environment than those operating at conventional 25 temperatures of less than 100°C.

While the coolant compositions of this invention are particularly suitable for use in a process for cooling in internal combustion engines, they are also 30 usefully employed in other applications such as heat-transfer fluids or hydraulic fluids.

Alkylene glycols suitably employed as the coolant in the compositions of this invention are those dihydric alcohols which are liquid at temperatures in

the range of -65°C to -30°C and which boil at atmospheric pressure at temperatures in the range from 150°C to 230°C. Examples of such glycols include ethylene glycol, propylene glycol, glycerol and mixtures of two or more thereof in any proportion.

5 Preferred glycols are ethylene glycol, propylene glycol and mixtures thereof. More preferably, the alkylene glycol is propylene glycol or a mixture of at least 30 weight percent of propylene glycol and from 0.1 to 70 weight percent of ethylene glycol. Use of propylene glycol is most preferred.

10 The corrosion inhibitor combination employed in the coolant composition suitably comprises and 15 preferably consists essentially of (a) from 0.06 to 0.5 weight parts of the azole, (b) from 0.1 to 0.2 weight parts of the molybdate salt and (c) from 0.05 to 0.09 weight parts of phosphoric acid.

20 A suitable corrosion - inhibiting amount of the inhibitor combination may be determined empirically by use of standard corrosion tests with samples of varied quantities of the inhibitor combination. Since some 25 users may ascribe greater importance to one test than another, the significance of corrosion testing is relative and not absolute. However, the ASTM test methods described in the working examples are commonly employed.

30 Typically, in the total coolant composition, from 0.05 to 2 weight percent of the inhibitor combination is suitable and preferably from 0.1, more preferably 0.25 up to 1, more preferably 0.75 weight percent of the inhibitor combination is employed.

The azole which is used in the practice of this invention is any azole which is soluble in the alkylene glycol and which is a corrosion inhibitor for copper and brass. The azole is preferably a triazole such as tolyltriazole, benzotriazole and mixtures of two or 5 more thereof. Tolyltriazole is most preferred. Other azoles which are suitable but less preferred than the aforementioned triazoles include thiazoles such as mercaptobenzothiazole, and alkali metal salts of such 10 azoles.

Molybdate salts employed in the inhibitor combination are those which are soluble in the alkylene glycol and which are corrosion inhibitors for steel and 15 cast iron. Such salts include the molybdates of the alkali metals and alkaline earth metals. Examples of preferred molybdates are sodium molybdate, ammonium molybdate, potassium molybdate and mixtures of two or more thereof. Sodium molybdate is most preferred. 20

The phosphoric acid is employed to maintain the pH of the coolant composition in the range from 7 to 9, preferably from 7 to 8, and only if necessary. Some 25 alkylene glycol mixtures are within the pH limits, and in such cases no pH adjustment is required.

The coolant composition of this invention is prepared by first dissolving up to 10 weight percent of 30 water in the alkylene glycol. Preferably less than about 5 weight percent and more preferably about 3 percent of water is dissolved in propylene glycol. Most preferably the alkylene glycol is used with essentially no water, i.e., less than about 1 weight percent. Subsequently, the corrosion inhibitor

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combination is dissolved into the alkylene glycol composition. Preferably, the resulting coolant composition is then rendered basic by adding sodium or potassium hydroxide until a pH of from 7 to 9 is reached, or phosphoric acid is added if the initial pH 5 value of the alkylene glycol base fluid is too alkaline. Optionally other ingredients such as dyes and antifoaming agents, e.g., those disclosed in U.S. Patents 3,340,309; 3,504,041; 3,770,701 and 10 2,425,755, can be added to the composition. While anti-foam additives are not required, they may nevertheless be employed.

The process of cooling an internal combustion 15 engine is carried out by circulating the coolant composition of the invention through the cooling jacket of the engine. The invention composition is designed to be used "as is", i.e. a full fill coolant, in cooling equipment such as described in U.S. Patent 20 4,550,690 previously mentioned, at ambient pressures, e.g. atmospheric pressure, yet to avoid corrosive effects on the metal components of such cooling equipment by use of the carefully chosen corrosion inhibitor combination.

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The cooling process is preferably carried out at a coolant operating temperature range of 105°C to 150°C, temperatures previously noted above. More 30 preferably the operating temperature range of the coolant is above 110°C, most preferably above 120°C and more preferably below 140°C, most preferably below 135°C.

Preferably the coolant composition contains not more than 5 weight percent, more preferably not more

than 3 weight percent and most preferably not more than 1 weight percent water.

The preferred composition of the corrosion inhibitor package is the same as previously noted above 5 and most preferably consists essentially of an azole, a molybdate salt and optionally the phosphoric acid when pH adjustment is desired. The amounts of each component to be employed are also noted previously in the text.

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The following examples are given to illustrate the invention and should not be construed as limiting its scope. Unless otherwise indicated, all parts and percentages are by weight.

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Examples 1-2

A coolant concentrate is prepared by dissolving 20 about 1 part of tolyltriazole, about 0.6 part of sodium molybdate dihydrate and about 0.3 part of an 85 percent solution of phosphoric acid in water, in 20 parts of propylene glycol containing 4 parts of water. The resulting concentrate is then combined with 370 parts 25 of propylene glycol to form the coolant composition which has a pH (100-ml sample diluted 1:1 in water) in the range from 6 to 7. The anhydrous coolant composition is then tested for corrosion inhibition. The resulting coolant's composition is described in and 30 the test results are reported in Table I.

An additional coolant composition (Example No. 2) is similarly prepared using a mixture of ethylene glycol and propylene glycol as the alkylene glycol blend. This composition is similarly tested for cor-

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rosion inhibition. The coolant's composition and the results of these tests are also reported in Table I.

For purposes of comparison, a control coolant composition is prepared using propylene glycol (Example 5 No. C₁) and 30/70 mixture of uninhibited propylene glycol and ethylene glycol (Example No. C₂). These compositions are also tested and the results of those tests are also reported in Table I.

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TABLE I

<u>Example No.</u>	<u>1</u>	<u>2</u>	<u>C₁*</u>	<u>C₂*</u>
Glycol ^① , wt pts				
PG	100	30	100	30
EG	0	70	0	70
Water, wt pts	1	1	<1	<1
Azole ^② , wt pts				
TT	0.25	0.25	0	0
Molybdate, wt pts				
Na ₂ MoO ₄ ·2H ₂ O	0.15	0.15	0	0
H ₃ PO ₄ (85%)	0.075	0.075	0	0

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TABLE I (cont'd)

<u>Example No.</u>	<u>1</u>	<u>2</u>	<u>C_{1*}</u>
Corrosion Inhibition, wt loss in 336 hours			
Glassware® Corrosion, mg wt loss**			
Cu	13.7	1.9	8.8
Solder	9.0	41.8	93.2
Brass	0.6	1.1	104.3
Steel	0.5	+6.5	239.8
Mg	1.3	1015.5	>2000.0
Al	0.3	+11.1	+0.7
wt loss in 336 hours			
Glassware® Corrosion, mg wt loss**			
Cu	0.5	1.9	36.5
Solder	6.6	31.2	868.3
Brass	0.0	0.7	17.8
Steel	+0.1	0.0	21.8
Cast Iron	+0.2	+0.4	5.0
Al	0.3	+0.2	+6.8

TABLE I (cont'd)

Example No.	1	2	<u>C₁</u> *	<u>C₂</u> *
Corrosion Inhibition, Heat Rejecting Metal Surface Test ^① , weight loss, mg/cm ² /week (168 hr)				
Al	0.085	-	0.67	0.21
Mg***	0.19	2.77	5.79	-
Engine Dynamometer Corrosion Test ^② , mg wt loss**				
after 672 hours				
Cu	24.0	-	-	-
Solder	8.6	-	-	-
Brass	1.3	-	-	-
Steel	0.6	-	-	-
Cast Iron	0.0	-	-	-
Al	0.6	-	-	-

* Not an example of the invention

** Weight loss in milligrams is measured using a standard coupon for the test having an area 5 cm by 2.5 cm (2 inches by one inch)

*** Same method as used for Al except Mg coupon is cleaned with 20% chromic acid in place of the 28 chromic acid - 5% orthophosphoric acid mixture of ASTM D-4340,

① PG - propylene glycol, EG - ethylene glycol

② TT - tolyltriazole

③ ASTM D-1384

④ ASTM D-4340 - modified to use neat fluid, without ASTM corrosive water.

⑤ Engine dynamometer test using a Ford Escort 4-cylinder engine operating at a ΔT of 19.4°C (35°F) across the radiator and at a ΔT of 8.3°C (15°F) across the heater core and overall average engine operating temperature of 107°C (225°F).

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As evidenced by the data set forth in Table I, the coolant compositions of this invention exhibit good corrosion inhibition for both aluminum and magnesium when the coolant compositions are exposed to temperatures in excess of 105°C for periods up to 672 hours.

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CLAIMS :

1. A coolant composition comprising (1) at least 90 weight percent of an alkylene glycol or a mixture of two or more alkylene glycols and (2) a corrosion-inhibiting amount of an inhibitor comprising
5 (a) from 0.02 to 4 weight parts of an azole, (b) from 0.05 to 3 weight parts of a molybdate salt and (c) from 0 to 3 weight parts of phosphoric acid.

10 2. The composition of Claim 1 wherein the alkylene glycol is propylene glycol or a mixture of at least 30 weight percent of propylene glycol and from 0.1 to 70 weight percent of ethylene glycol.

15 3. The composition of Claim 2 wherein the composition contains no more than 5 weight percent of water.

20 4. The composition of Claim 2 wherein the composition contains no more than 1 weight percent of water.

5. The composition of Claim 4 wherein the alkylene glycol consists solely of propylene glycol.

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6. The composition of Claim 2 wherein the azole is a triazole.

7. The composition of Claim 6 wherein the triazole is tolyltriazole, benzotriazole and mixtures thereof.

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8. The composition of Claim 2 or 4 wherein the azole is tolyltriazole.

10 9. The composition of Claim 6 wherein the azole is mercaptobenzothiazole.

15 10. The composition of Claim 2 wherein the molybdate salt is an alkali metal molybdate.

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11. The composition of Claim 2 or 4 wherein the molybdate salt is sodium molybdate.

12. The composition of Claim 5 wherein are 20 present (a) tolytriazole, (b) sodium molybdate and (c) phosphoric acid in the respective amounts of (a) 0.25, (b) 0.15, and (c) 0.075 percent by weight of the composition.

25 13. A process for removing heat generated in the operation of an internal combustion engine by circulating through the cooling jacket of said engine, a coolant which is exposed to approximately the ambient pressure of the surrounding environment at a coolant 30 operating temperature above 105°C, having the improvement of employing as said coolant a liquid composition having low corrosivity toward the materials of construction with which said coolant is in contact,

which composition is the coolant composition defined by
Claim 1.

14. The process of Claim 13 wherein the
alkylene glycol consists essentially of propylene
glycol or a mixture of at least 30 weight percent
5 propylene glycol and from 0.1 to 70 weight percent
ethylene glycol and the coolant composition contains no
more than 5 weight percent water.

10 15. The process of Claim 14 wherein the
coolant composition contains no more than 1 weight
percent water and the alkylene glycol consists solely
of propylene glycol.

16. The process of Claim 14 or 15 wherein
15 (a) the azole is tolyltriazole
(b) the molybdate is sodium molybdate.

17. The process of Claim 14 or 15 wherein
20 (a) the azole is tolyltriazole present in
0.25 weight percent,
(b) the molybdate is sodium molybdate
present in 0.15 weight percent and
(c) phosphoric acid is present in 0.075
25 weight percent, of the composition
weight.

18. The process of Claim 14 or 15 wherein the
coolant operating temperature is normally in the range
30 between 110° and 140°C.

INTERNATIONAL SEARCH REPORT

International Application No. **PCT/US89/01544**

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC (4): C09K 5/00

U.S. CL. 252/75

II. FIELDS SEARCHED

Minimum Documentation Searched ⁷

Classification System	Classification Symbols
U.S.	252/74, 75, 77
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸	

III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	US, A, 4,440,721, (Wilson et al), 04 April 1984, (Note the entire document)	1-18
Y	US, A, 4,450,088, (Wilson et al), 22 May 1984, (Note column 3, lines 32-42)	2,5,14,15
Y	US, A, 4,382,870, (Abel et al), 10 May 1983, (Note column 2, lines 1-4)	2,5,14,15
Y	US, A, 4,550,694, (Evans et al), 05 November 1985, (Note Abstract)	13
Y	US, A, 4,630,572, (Evans et al), 23 December 1986, (Note Abstract)	13
Y	Derwent Abstracts, Accession Number 83-811019/45, "Corrosion Inhibitor for Aluminum in Engine Cooling System"; corresponds to Japanese Patent J58164792-A 29 September 1983, (Note Abstract)	1,6-8,10-12

* Special categories of cited documents: ¹⁰

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IV. CERTIFICATION

Date of the Actual Completion of the International Search

06 June 1989

Date of Mailing of this International Search Report

17 JUL 1989

International Searching Authority

Signature of Authorized Officer

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